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Monitoring for Polychlorinated Biphenyl Emissions from an Electrolytic Capacitor Disposal Project

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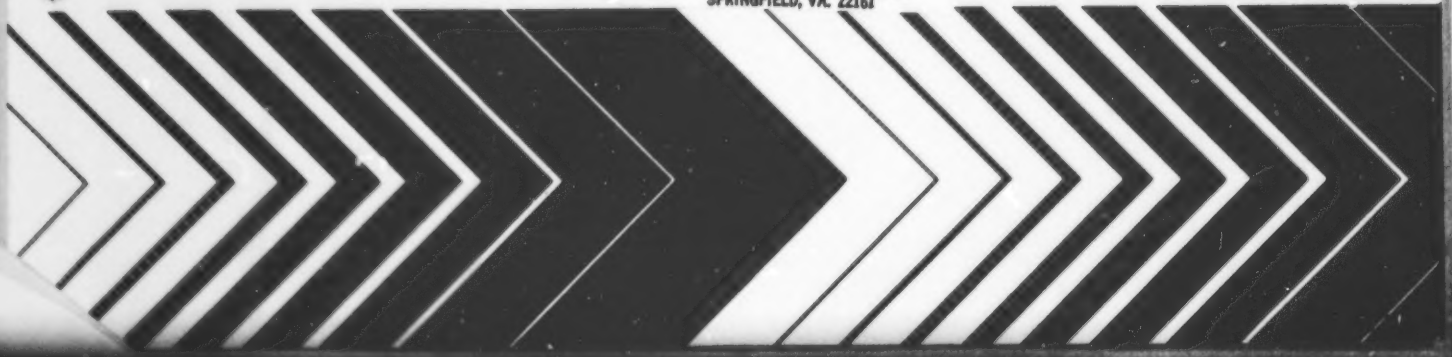

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MONITORING FOR POLYCHLORINATED BIPHENYL EMISSIONS FROM AN ELECTROLYTIC CAPACITOR DISPOSAL PROJECT

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ABSTRACT

Three different air sampling methods were used simultaneously to monitor for polychlorinated biphenyl (PCB) emissions arising from a pilot disposal project involving electrolytic capacitors. Analytical results indicated that the primary PCB material was Aroclor 1242, and that airborne concentrations inside the building housing the grinders exceeded 5 mg/m^3. The PCB air concentrations outside the building at a distance of 9 m were typically <1.0 $\mu g/m^3$. Measurements made with one low-volume and two high-volume air samplers are compared.

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SECTION 1

INTRODUCTION

In late March 1976, the U.S. Environmental Protection Agency (EPA) undertook a monitoring project to determine the extent of air pollution associated with a pilot-scale disposal of electrolytic capacitors in El Dorado, Arkansas. The proposed full scale disposal operation was to have consisted of pulverizing, then incinerating electrolytic capacitors. It was suspected that, during the grinding operation, polychlorinated biphenyls (PCBs) would be emitted, which could pose a potential health hazard. The capacitors were known to contain an Aroclor dielectric liquid, although the exact mixture was not identified.

At the inception of the study, several air sampling methodologies for PCBs were known to be in the developmental stages. However, no method had been evaluated sufficiently to suggest its exclusive selection for use. It was decided, therefore, to employ three different methods simultaneously to provide corroborating data. It was also felt that valuable comparisons could be derived from this approach.

SECTION 2

SAMPLING METHODOLOGY

The three methods selected were: (a) a modified high volume (Hi-Vol) sampler under evaluation by the Office of Toxic Substances (OTS) of EPA (1); (b) a modification of the Hi-Vol sampler designed for EPA by Syracuse University Research Corporation (SURC) to monitor airborne pesticides (2); and, (c) the low-volume pesticide air sampler marketed by Micro-chemical Specialties Company (MISCO), Berkeley, California. The latter device has been widely used by EPA and others to sample ambient air for pesticides and PCBs (3).

METHOD I

The OTS sampling method for PCBs is based on polyurethane foam collection but uses a standard Hi-Vol head with an extended throat (Figure 1). The sampler is operated as a standard Hi-Vol with the addition of a plug of foam 90 mm (3.5 in.) in diameter and 76 mm (3 in.) in length which is placed into the 15-cm (6 in.) throat extension. A standard 20.4- by 25.5-cm (8- x 10-in.) glass fiber filter is used as a prefilter. The addition of the foam plug reduces the normal flow rate to 0.70-0.85 m^3/min (25-30 ft^3/min). No mention is made in the OTS procedure (1) concerning changing of the inlet opening to provide dynamic similarity with the standard Hi-Vol.

METHOD II

The SURC sampler is a substantially modified Hi-Vol sampler utilizing a special glass collection module attached to a standard Hi-Vol vacuum blower. The glass module is assembled from commercially available process glass pipe and is basically a 10- by 5-cm reducing section with stainless steel screens

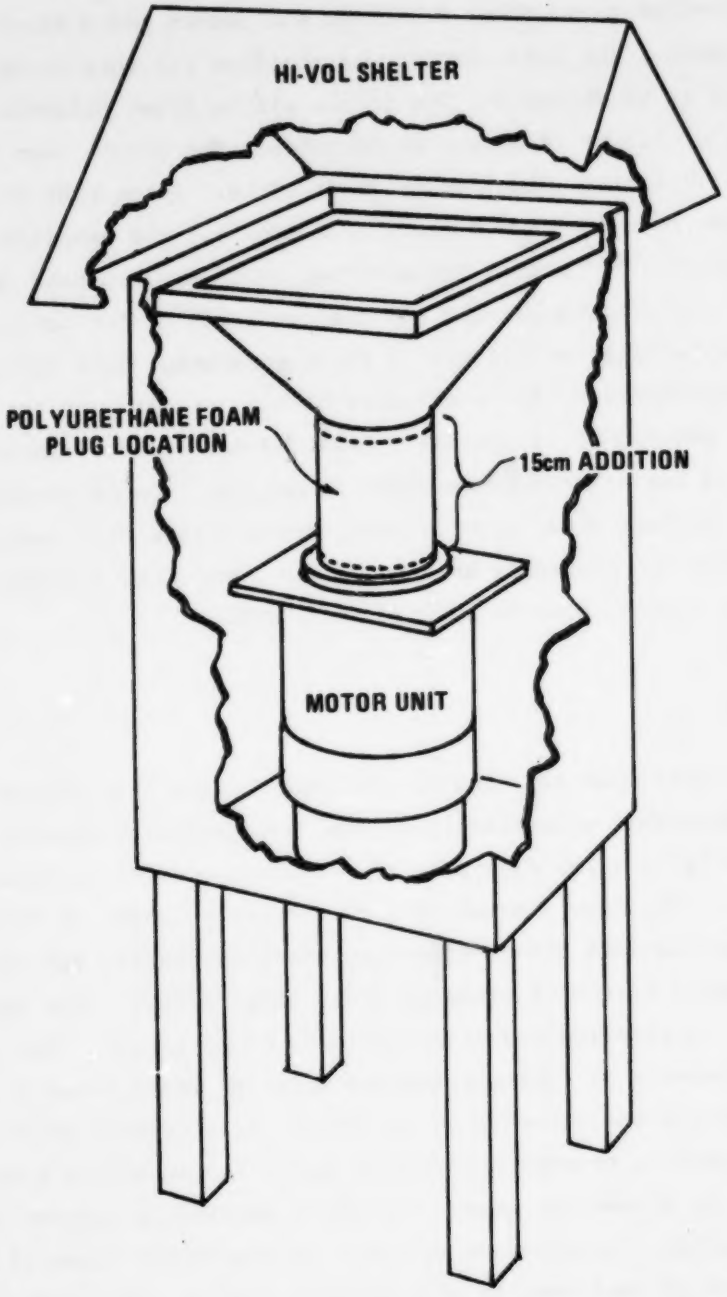

Figure 1. Diagram of OTS sampler (Method I).

to support a circular glass fiber filter at the intake and a vapor trap in the smaller chamber. The SURC sampler was modified for this study and is shown schematically in Figure 2. The intake air is first filtered through a glass fiber filter 115 mm (4.5 in.) in diameter. The air is then filtered through a 58 mm (2.25 in.) diameter by 76 mm (3 in.) thick plug of polyether-type polyurethane foam (average density 0.02 g/cm^3). The sampling rate is 0.20-0.22 m^3/min (7-3 ft^3 min). The modified SURC samplers used for this study have an annulus inlet space (around the shelter roof) of 0.5 cm (0.2 in.) to provide an inlet velocity of 0.6 m/s (2 ft/s) consistent with the Federal Register (4) specifications for a standard Hi-Vol, except that the shelter (General Metals GMW-65000) is specially designed for ease in sample changing. The sampler has a Dixon pressure recorder to monitor flow performance continuously and a venturi meter to provide a more accurate flow measurement. These samplers are not presently available from commercial sources. The cost of materials for construction is approximately $600.

METHOD III

The general pesticide air sampler designed for the U.S. Public Health Service (3) is available commercially as the MISCO Model 88 sampler. This sampler is essentially a low flow rate (0.017-0.020 m^3/min) impinger system with a prefilter. The flow diagram of this sampler is shown in Figure 3. The impingers are standard 500-ml Greenburg-Smith impingers, and the prefilter is a 78 mm (3 1/16 in.) diameter glass fiber filter. The absorbing medium is 100 ml of preextracted high-purity ethylene glycol. The sampler is designed for gaseous or fine particulate sampling only, since no attempt is made to size-fraction the aerosols at the inlet, or to sample isokinetically. This inlet arrangement, however, provides a means for attaching a short line for sampling air in a specific area. The MISCO sampler is capable of operating four separate impingers in sequence by means of a built-in timer if desired. Parallel operation of impingers is also possible but at lower flow rates.

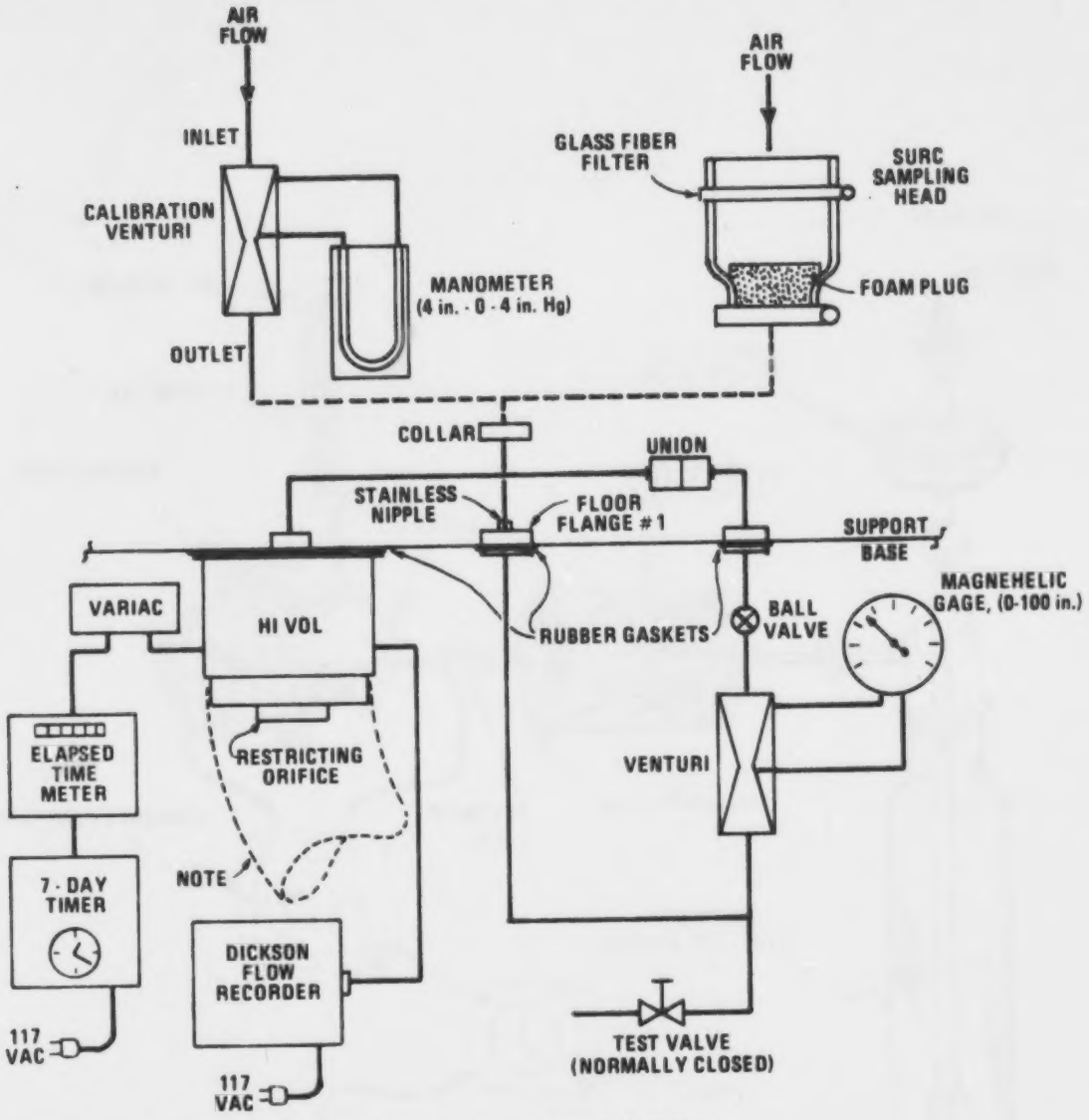

Figure 2. Schematic diagram of modified SURC sampler (Method II).

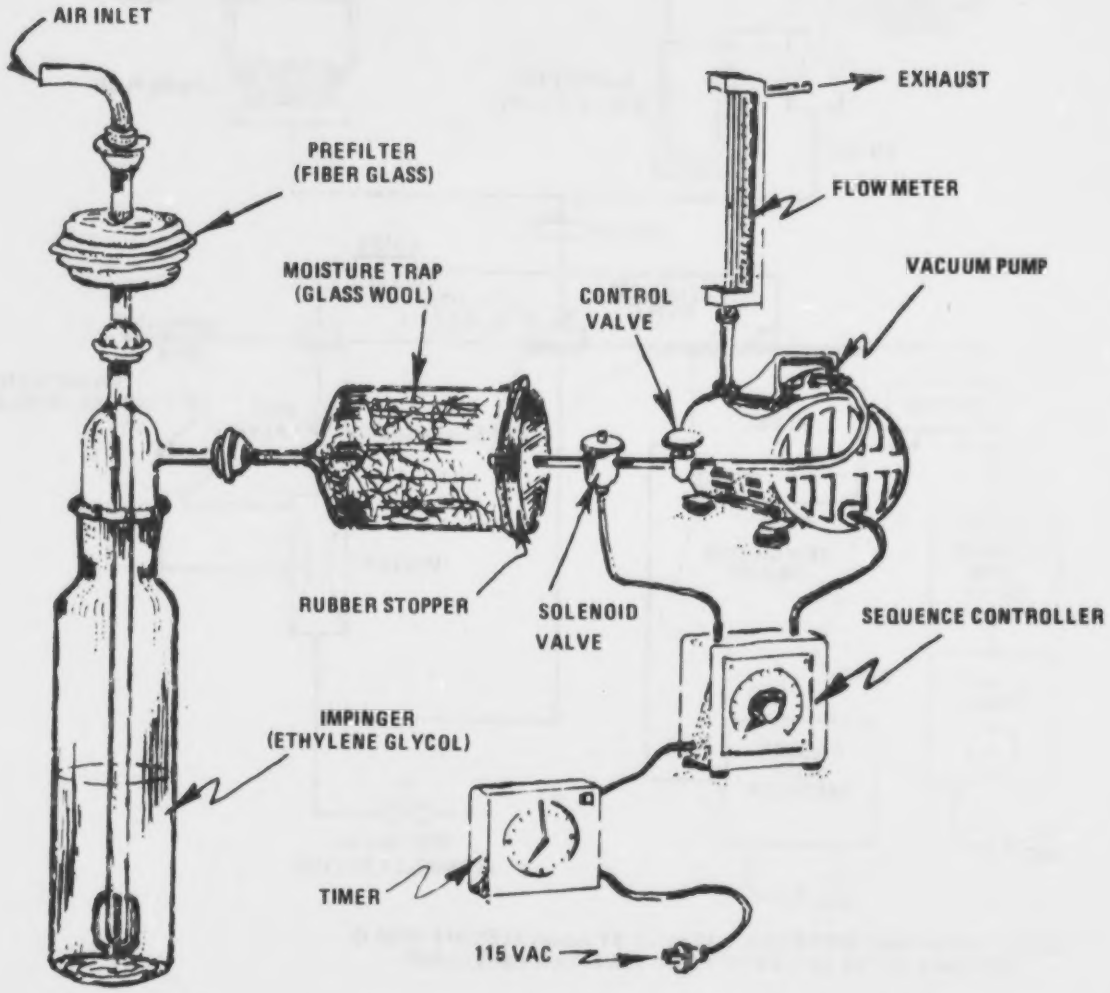

Figure 3. Schematic diagram of MISCO sampler (Method III).

Quality assurance measures employed during the sampling program were concerned primarily with flow measurement since this is the critical parameter in integrated sampler performance. All samplers were calibrated in the laboratory and referenced to a calibrated Rootsmeter. After setup in the field, audit devices (calibrated against the lab standard) were utilized to check the sampler calibrations and for recalibration if necessary. A calibration plot for the modified SURC sampler is shown in Figure 4. The SURC sampler provided two independent measurements of flow rate, one of which was a flow recorder to provide a permanent record. A programmable calculator/plotter was used to provide an exponential regression fit with associated statistics used to control the degree of scatter acceptable in a given calibration. After the sampling was completed, all samplers were rechecked for possible changes in flow calibration.

Potentially interfering background contaminants were removed from the collection media by chemical extraction prior to deploying the samplers in the field. The foam plugs were preextracted by successive 12-h Soxhlet extraction with acetone and hexane (5). The ethylene glycol used was purified by successive extractions with dichloromethane.

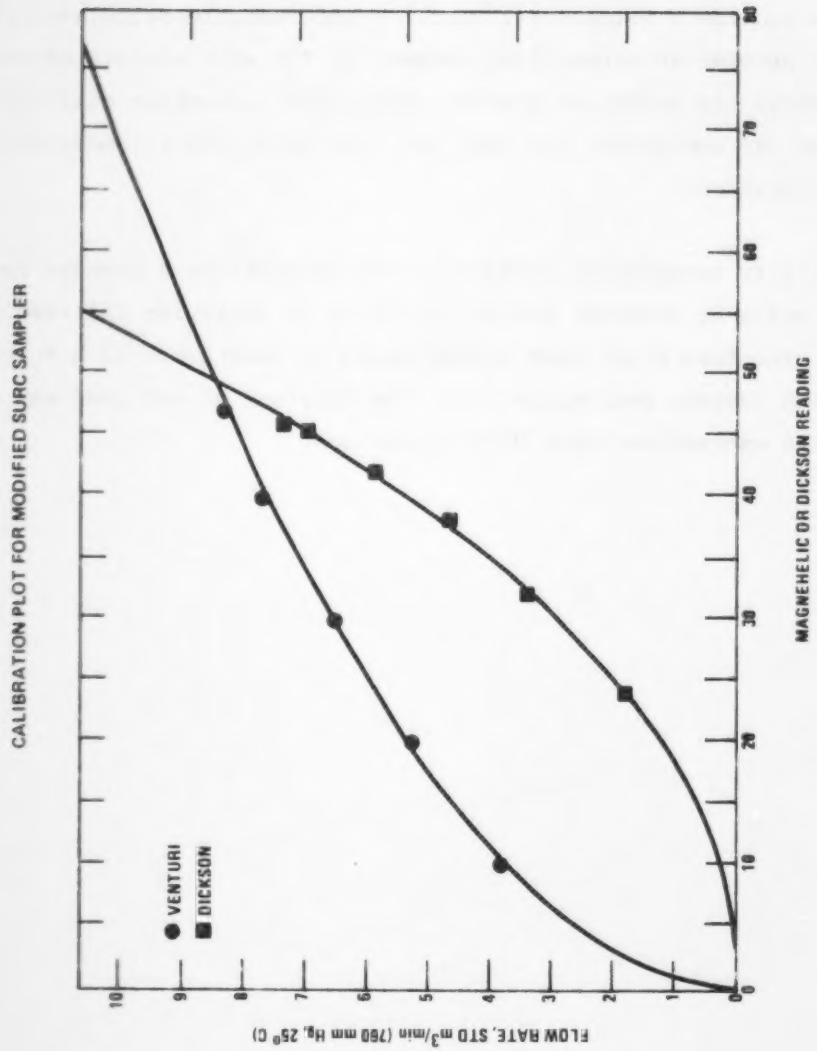

Figure 4. Calibration plot for modified SURC sampler.

SECTION 3

FIELD STUDIES

The capacitor disposal operation was conducted by Pollution Controls, Inc., El Dorado, Arkansas, under subcontract to TRW, Inc. TRW was under contract to the EPA Solid Waste Program to gather data on a variety of solid waste incineration methods. There were approximately 4500 kg (10,000 pounds) of discarded capacitors to be pulverized and ultimately incinerated in this test program. The pulverizing equipment consisted of two hammer-mills to handle both large and small capacitors. The hammer-mills had collection boxes into which the pulverized product was collected. After processing, special plastic-lined shipping containers were provided for the storage and shipment of the PCB-coated pieces.

The site location was an abandoned oil refinery in El Dorado. A detailed map of the site area and location of the concrete pad on which the grinders were located is shown in Figure 5. In order to study the prevailing winds, background meteorological measurements (wind speed and direction) were made from May 16 through May 18, 1976, to determine whether there was a prevailing wind direction. The data for this period indicated a general wind direction from the southeast. Because of the wind direction variability, however, it was decided to orient the samplers according to the wind direction just prior to grinding. During this background period, several sets of background samples were collected using the three sampling methods.

After the samplers were set up in the arrangement shown in Figure 5, the Arkansas Pollution Control Authority concluded that the grinders should be enclosed. Accordingly, a 3.6- by 5.5-m (12- by 18-ft) temporary building was constructed around the grinders. Enclosing the samplers resulted in two

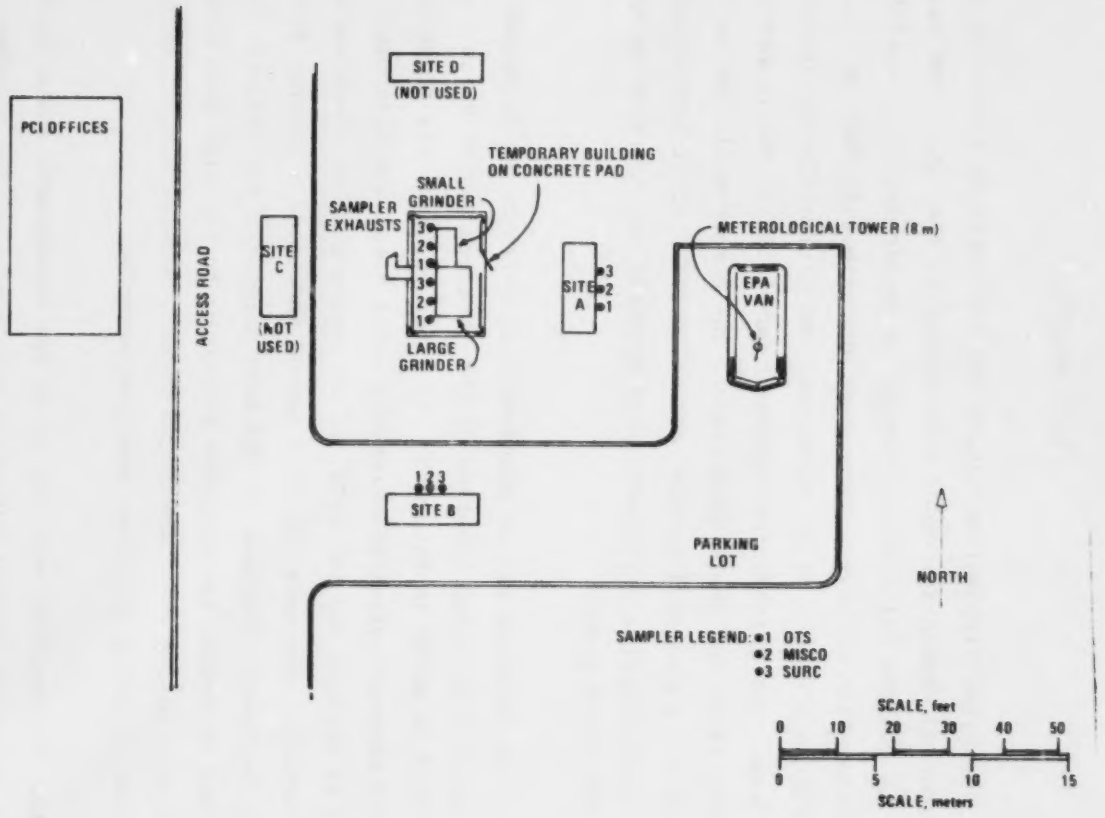

Figure 5. Sampling site in Eldorado, Arkansas.

problems: (a) how to protect the grinder operators inside the building from the expected higher local PCB emissions; and, (2) whether pseudoemission measurements inside the building could be made with the air samplers. In order to resolve the first problem, self-contained oxygen breathing canisters and protective clothing were provided for the two operators. Two of each type of sampler were placed inside the building. Special ducts were provided for the modified SURC and OTS samplers to exhaust the samplers outside the building. Because of the high total sampling rate of the six samplers (2.5 m^3/min), it was estimated that the entire volume of air inside the building would be exhausted every 30 min. In order to verify that a negative draft existed inside the building, a smoke bomb was set off outside the building. Unfortunately, an undesirable residue from the smoke test was deposited on the inside of the samplers, which subsequently posed some problems in sample analysis.

The capacitors were ground in a 35-min test run, then for 5 h of full scale operation. Because of the elevated temperature inside the building during daylight hours, the grinding was carried out only at night. Since the meteorological data (Table 1) during the majority of the grinding period indicated calm wind speeds and absence of a predominant wind direction, only background samplers at Sites A and B were operated.

TABLE 1. METEOROLOGICAL DATA DURING CAPACITOR GRINDING - 5/20/76

Time Interval	Wind Direction	Wind Speed, mph	Relative Humidity, %
0300-0400	-	calm	100
0400-0500	-	calm	100
0500-0600	-	calm	100
0600-0700	-	calm	100
0700-0800	50°	1.0	100
0800-0900	130°	2.0	83

Visual inspection through an observation port revealed very dense clouds of aerosol emitted from the grinders during operation. Some of this aerosol apparently emitted in large diameter (>100 μm) droplets, since the fog dissipated rapidly after the grinders were turned off. An odor characteristic of Aroclors was very pronounced in the building after grinding; subsequent analyses showed that all equipment inside the building, including the housings, was coated with this material. A sample of the capacitor grindings was collected for identification of the type of PCB mixture present.

SECTION 4

SAMPLE ANALYSES

Upon return to the laboratory, the 14 OTS, SURC, and MISCO sample sets (filter and vapor trap) were prepared for analysis. Due to the difficulty of the analysis, only six sample sets were examined. The samples selected included one from each of the three sampling methods located inside the building adjacent to the grinder and simultaneously outside at Site A (see Figure 5). The remaining samples were stored in a light-tight thermally insulated storage container.

Analysis of the capacitor grindings collected on-site to verify the type of PCB present established that the dielectric fluid used was Aroclor 1242, a PCB mixture containing 42% chlorine and consisting primarily of di-, tri-, and tetrachlorobiphenyls (v.p. ~0.001 mm Hg). Each sample consisted of two glass fiber filters (one representing the first 35 min of the collection cycle and the other the remaining 300 min) and one polyurethane foam plug or ethylene glycol sorbent. All samples showed gas chromatographic patterns which closely or exactly matched that of Aroclor 1242.

Two extraction methods were required for recovery of PCBs. Foam plugs and glass fiber filters were separately extracted for 24 h each with 700 ml of 5% diethyl ether in hexane in Soxhlet extractors. The extract was reduced to 1 to 2 ml in a Kuderna-Danish (KD) concentrator for cleanup on 10 cm x 7 mm (i.d.) alumina column (activity grade 4, 6.5% water). The fraction eluted from the column with 12 ml of hexane was then analyzed by electron gas chromatography (EC-GC). The ethylene glycol was diluted to 450 ml with water (3.5:1) and extracted three times in a separatory funnel with a total of 300 ml of hexane. The hexane was concentrated to 10 ml in a KD concentrator and subjected

to Florisil column chromatography according to the EPA Manual of Analytical Methods (6). Only fraction I (which contained the PCBs) was collected, concentrated to 1 to 2 ml, and analyzed by EC-GC.

GC analysis was carried out on a 138 cm x 6 mm (i.d.) glass column packed with 1.5% OV-17/1.95% OV-210 on 80-100 mesh Gas Chrom Q at 180°C. A ^{3}HSc electron capture detector was used for detection. Quantification was based on comparison of the sum of the heights of the 15 major chromatographic peaks in a standard of Aroclor 1242 with the corresponding peaks in the sample. (All 15 peaks were present in every sample.) Since only Aroclor 1242 was found in the capacitor fluid and all samples appeared to contain only this mixture, confirmation by mass spectrometry or perchlorination was deemed unnecessary.

Recoveries of Aroclor 1242 from polyurethane foam and ethylene glycol were determined to be 96%, and 98%, respectively, by analysis of spiked media. Therefore, it was not necessary to correct analytical data for losses in the analytical scheme. Sampling efficiencies could not be determined because of the multiplicity and complexity of the sampling procedures used. However, the 24-h collection efficiency for Aroclor 1242 vapors by polyurethane foam in the modified SURC sampler has been shown (5) to be 70-80% for effective air concentrations of 18-98 ng/m^3 sampled at 225 l/min.

The physical state of the airborne PCB mixture was apparently mostly liquid aerosol inside the grinding shed, while both particulate and vapor forms appeared to be present in the air outside the building. Sampling efficiencies, therefore, may have varied widely for each sampler and at the two sites.

Blank values for filters, foam, and ethylene glycol carried to the sampling site in sealed containers and returned for analysis showed only minimal contamination by Aroclor 1242 (<0.3 to 8.8 µg per sample). These values corresponded to air concentrations of 0.007 to 1.1 µg/m^3, depending on the sampler used, and were not used for data correction.

SECTION 5

RESULTS AND DISCUSSION

Sample identifications and analytical results are presented in Table 2. Total air concentrations of Aroclor 1242 as determined by the three samplers appear to be in reasonably good agreement except in the case of sample No. 6 (MISCO sampler, site A). Sample contamination is thought to be the cause of the relatively high value of this sample. Lowest values were obtained with the OTS sampler (Method I) at both sites and may reflect poorer sampling efficiency. Disagreement existed between Methods I and II as to the relative amounts of material collected by the filters and foam plugs. Since the two samplers are very similar in design and have similar air volume-to-filter surface area ratios (2 l/min-cm^2 for OTS, 2.8 l/min-cm^2 for the modified SURC), similar collection efficiencies would be expected. The relatively high proportion of PCB material collected by the foam vapor trap of the modified SURC sampler may be due in part to leakages observed around the prefilter. Substantial vaporization from the prefilter to the foam trap would be expected for both Method I and II samplers, however. No satisfactory explanation could be made for the lack of PCB material in the Method I foam trap.

The levels of PCB measured inside the building were much higher than expected, which demonstrated that uncontrolled grinding emissions may pose a substantial "in-plant" health hazard. By comparison, the 8-h NIOSH occupational standard is set at 1 mg/m^3 for Aroclor 1242 (7). Since the collection capabilities of the sampling methods may have been exceeded at the mg/m^3 level, the measured concentrations inside the building may have been even higher than indicated. The outside levels of <1 $\mu g/m^3$ during grinding were probably much higher than the true background that existed before grinding began, although no pregrinding background samples were analyzed. Because of the large dif-

ferences between inside and outside measurements during grinding, the magnitudes of the three background samples become relatively unimportant. If resources permit, further analyses of the stored samples may be attempted at a later date to obtain information on the reproducibility of a given sampling method. Cross-contamination and sample loss during storage could, however, complicate interpretation of the low level results.

TABLE 2. ANALYSIS DATA SUMMARY - EL DORADO, ARKANSAS, PCB STUDY

Sample No.	Site	Method	Prefilter Collection* ($\mu g/m^3$)	Foam/Glycol† Collection ($\mu g/m^3$)	Total Collection ($\mu g/m^3$)
1	E	I	1848	trace	1848
2	E	II	762‡	5070	5832
3	E	III	28‡	5210	5238
4	A	I	0.62	0.03	0.65
5	A	II	0.16	0.69	0.85
6	A	III	0.84	7.52	8.36

*Concentrations expressed as $\mu g/m^3$ Aroclor 1242.
†Method I and II used polyurethane foam; Method III used ethylene glycol as second collection stage.
‡Indications of leakage by prefilter.

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